

that the difference is just compensated by the effect of a statistical distribution. In that case one might expect that at room temperature the thermal motion of the atoms of the iodine molecules would be appreciably larger than that of the atoms of the triiodide ions. From $(F_o - F_c)$ syntheses of the projections at room temperature it was shown, however, that the temperature factor of none of the iodine atoms differed significantly from the mean B value, 5.2 \AA^2 , although the estimated standard deviation in the B values was not larger than about 0.12 \AA^2 .

Therefore an average structure of $\text{N}(\text{C}_2\text{H}_5)_4\text{I}_7$, in which only the asymmetrical I_3^- ions are statistically distributed, does not seem to be very likely. The possibility of an average structure, involving equally the triiodide ions and the iodine molecules, possibly in connection with the two alternative orientations of the $\text{N}(\text{C}_2\text{H}_5)_4^+$ ions, cannot be excluded.

A theoretical discussion of the bonds in polyhalogen compounds by the LCAO method has been given elsewhere (Havinga, 1957). It was shown that centrosymmetrical triiodide ions may be expected and that the deviation from centrosymmetry in compounds like CsI_3 may be explained by the interaction of the cations and anions.

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Short Communications

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The crystal structures of ThHg_3 , ThIn_3 , ThTl_3 , ThSn_3 and ThPb_3 . By RICCARDO FERRO, *Chemical Institute, Laboratory of Physical Chemistry of Genoa University, Genoa, Italy*

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The compound ThHg_3

The compound ThHg_3 has been prepared and studied by Baenziger, Rundle & Snow (1956). They found that it is closed-packed hexagonal with $a_1 = 3.38$ and $a_3 = 4.72 \text{ \AA}$, and they do not exclude the possibility of solid-solution formation. The present author has found the same structure but has obtained slightly different values for the unit-cell edges; he has not succeeded in observing the formation of solid solutions. Several samples containing a variable mercury content around that of ThHg_3 (Th% theor. = 27.83) have been prepared. Two samples, which when analyzed were found to have a Th content of 27.3 and 28.5% respectively, have shown Debye lines which are characteristic of the ThHg_3 phase. The same reflexions with the same values for the lattice parameters have also been observed (both alone and mixed with the

lines of other phases) in other samples containing quantities of Th a little higher or a little lower.

The constants (obtained by the Straumanis powder method, with $\text{Cu K}\alpha_1$ radiation $\lambda = 1.540500 \text{ \AA}$) are in Table I together with those of the isostructural LaHg_3 (Iandelli & Ferro, 1951) and UHg_3 (Rundle & Wilson, 1949):

Table I. *Lattice constants (\AA) and densities (g.cm.^{-3}) for isostructural compounds MeHg_3*

	LaHg_3	ThHg_3	UHg_3
a_1	3.411	3.364	3.327
a_3	4.961	4.907	4.888
a_3/a_1	1.454	1.459	1.469
ρ_x	12.30	14.39	14.88

As we can observe, all the axial ratios are very similar.

The alloys were prepared in iron vessels, lined with a thin sheet of molybdenum and sealed by electric welding. The alloys were then heated up to 1000–1100 °C., stirred at this temperature (at which they seemed to be completely molten) and then cooled to room-temperature either quickly or very slowly. After cooling, the iron vessel was turned down in a lathe until there was just a thin metal layer left which was then taken completely off in a closed glass tube under a continuous circulation of dry CO₂. The alloy was crushed and was then allowed to fall into thin glass capillary (joined to the tube) which then, after welding with a flame, was used for the X-ray examination. It was necessary to work in the same way for taking samples for chemical analysis, because the alloys ignite immediately on contact with air.

For the analysis the samples weighed in vessels full of CO₂ were immediately covered with water (to avoid air oxidation) and were then treated carefully with HNO₃. After solution the mercury was precipitated as HgS and collected in a weighed Gooch crucible. In the filtrate the Th was determined as ThO₂ via the oxalate. Moreover, in the analysis of the above samples no appreciable quantities of either Fe, Mo, or ThO₂ were found.

The compounds ThIn₃, ThTl₃, ThSn₃ and ThPb₃

These compounds have been prepared by pressing together the powders of the two metals and by heating the compounds, sealed *in vacuo* in silica vessels, up to ca. 1000 °C. In order to obtain a well crystallized alloy it is necessary, specially for ThSn₃ and ThPb₃, to allow a rather long annealing at low temperatures (300–500 °C.).

The thorium used in the preparations was obtained by reduction of ThO₂ with Ca: its purity was about 99.7% (impurities were mainly represented by oxygen in the form of ThO₂). None of the other metals was below 99.9% purity.

The different alloys have been analyzed in the following way:

ThIn₃:

Solution in HNO₃, precipitation of In with H₂S, resolution of In₂S₃ and determination of In as In₂O₃. In the filtrate: determination of Th as ThO₂. Result: In 61.1₈%, Th 39.1₀% (theor.: Th% = 40.27).

ThTl₃:

Solution with HNO₃, precipitation of Th oxalate. In the filtrate, after reduction with SO₂, determination of Tl as TlI. Result: Tl 72.9₀%, Th 26.8₈% (theor.: Th% = 27.46).

ThSn₃

Treatment with HNO₃, filtration of the metastannic acid and its ignition to SnO₂. In the filtrate determination of Th. Determination of impurities of SnO₂ by volatilisation of Sn as SnI₄. Result: residue: 0.8%. On the remainder: Sn 60.6₅%, Th 39.2₅% (theor.: Th% = 39.46).

ThPb₃

Solution with HNO₃ and precipitation with H₂S. Solution of PbS and determination of Pb as iodate.

In the filtrate determination of Th as ThO₂ via the oxalate. Result: Pb 73.7₃%, Th 26.7₀ (theor.: Th% = 27.19).

The alloys obtained as described are rather oxidizable and the ones with heavier metals appear fairly pyrophoric; this fact can perhaps be related to what happens, for instance, with the elements of the 5th group where the thorium alloys with the heavier metal (bismuth) are also highly pyrophoric (Ferro, 1957) as contrasted with the more stable compounds with arsenic and antimony (Ferro, 1955, 1956).

Examination with X-rays shows that all the above compounds have a cubic structure of L12 type (Strukturbericht). Their constants are given in Table 2 together with those of the similar compounds of uranium (Iandelli & Ferro, 1952; Teitel, 1952; Frost & Maskrey, 1953–54).

Table 2. Lattice constants (Å) and densities (g.cm.⁻³) for MeX₃ compounds

	a_0	ρ_x		a_0	ρ_x
ThIn ₃	4.695	9.25	UIn ₃	4.597	9.95
ThTl ₃	4.748	13.11	UTl ₃	4.684	13.75
ThSn ₃	4.718	9.30	USn ₃	4.629	9.95
ThPb ₃	4.856	12.38	UPb ₃	4.797	12.93

General remarks

The molar volumes of all the above mentioned compounds are summarized in Table 3—both those obtained from the crystallographic data (V_M) and those obtained by adding the atomic volumes (ΣV_A). For the compounds of thorium there are considerable volume contractions while for uranium (whose atoms are smaller) the contractions (probably caused only by the other metals) are much lower. However, in both cases, a rather similar behaviour for the different compounds is observed.

Table 3. Molar volumes of the MeX₃ compounds (cm.³)

ThX ₃	ΣV_A	V_M	$\frac{\Delta V}{\Sigma V_A}$ %	UX ₃	ΣV_A	V_M	$\frac{\Delta V}{\Sigma V_A}$ %
ThHg ₃	63.0	57.9	8.0	UHg ₃	56.0	56.4	-1.0
ThIn ₃	66.9	62.3	6.9	UIn ₃	59.5	58.5	1.7
ThTl ₃	71.5	64.5	9.8	UTl ₃	64.1	61.9	3.4
ThSn ₃	68.7	63.3	7.9	USn ₃	61.3	59.7	2.6
ThPb ₃	74.6	69.0	7.5	UPb ₃	67.2	66.5	1.0

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